

A Comparison of Gas Chamber Tests of Bookbinding Leather With a Long Time Atmospheric Exposure

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ABSTRACT

Twenty-four samples of bookbinding leathers, tanned in various ways, have been exposed as bookbindings to atmospheric pollution for periods of 12 to 19 years. Physical and chemical tests made after exposure correlate reasonably well with gas chamber tests made on the leather before exposure.

INTRODUCTION

The deterioration of bookbinding, upholstering and similar leathers has been the subject of many investigations. A bibliography of some of this work is given at the end of the paper.

Veitch, Frey and Leinbach⁴⁴ in 1926, and Innes²² in 1930 published data indicating that the pick-up of sulfuric acid from polluted atmospheres was an important cause of the decay of leather bindings. This was confirmed in 1931 by Frey and Clarke¹⁶, who showed that leathers absorbed from the air the equivalent of 2 to 8 per cent sulfuric acid in about 8 years.

In previous work on the deterioration of bookbinding leathers we have used a gas chamber as a means of increasing the concentration of SO₂ gas in the atmosphere. Gas chambers had previously been used by Woodward⁴⁶, and Lamb³⁶.

In our original gas chamber¹⁷ pollution of the atmosphere was caused by a lighted gas jet burning continuously at the rate of 2.17 cubic feet per hour. The sulfur content of the gas was such that the gaseous sulfur products of combustion ranged from 0.00088 to 0.00101 grams per 100 liters of air, calculated as H₂SO₄. Under these conditions the deterioration or "red-rotting" of vegetable-tanned leathers in 12 to 18 weeks was strikingly similar to that obtained under natural conditions over several years. Results obtained by physical and chemical tests were also similar to those obtained with naturally deteriorated leather.

The pollution of the atmosphere in this type of chamber depends upon the sulfur content of the illuminating gas which varies widely from place to place. Therefore, a new type of gas chamber¹⁹ was devised in which the amount of pollution could be rigidly controlled. The pollution depended upon the

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burning of methanol containing dissolved amyl sulfite. A lamp was developed which gives a uniform sized flame at all times and which requires filling only once a week. For our work the lamp was adjusted to burn 95 grams of fuel in 24 hours, giving 1.78 grams SO_3 , and a concentration of SO_2 in the chamber approximately the same as in the illuminating gas chamber.

Innes, Mayer and Mitton have recently devised a gas chamber²⁶. This contains several modifications but the fundamental feature is the same as in our gas chamber, that is, the production of an SO_2 polluted atmosphere by the burning of a fuel containing sulfur in some form.

With our gas chamber we have determined the resistance to acid deterioration of leathers tanned by different tanning materials¹⁸, by straight chrome tannage¹⁷, and by combination tannages such as chrome and vegetable¹⁵ and vegetable and alum^{6, 19}. We have also determined the effect of adding materials to the leather such as sodium chloride, natural non-tannins and buffering salts¹⁸. We found that chrome-tanned leather was more resistant than vegetable-tanned. However, chrome-tanned leather is more empty, stretchy and resilient than vegetable-tanned; it resists wetting back uniformly with water and is difficult to dye and finish as compared with vegetable-tanned leather. These properties make it somewhat unsuitable for bindings. A combination chrome and vegetable tanned leather retains many of the desirable properties of vegetable-tanned leather and also has some of the acid-resistant properties of the chrome-tanned leather. Later it was found that vegetable leathers retanned with alum^{6, 19} were equally satisfactory.

For an evaluation of the value of the gas chamber tests, it was desirable to obtain a comparison of the results obtained by it, and those obtained by actual exposure. The results of such a test, requiring several years, are described in this paper.

EXPERIMENTAL

The experimental work was carried out in collaboration with the Government Printing Office. During the period from 1935 to 1941 twenty-four skins were obtained, tanned in various manners. Enough of each of these skins was cut out for exposure in the gas chamber, followed by physical and chemical tests. The remainder of each skin was then sent to the Government Printing Office where 3 volumes were bound with it. One set of these volumes was placed in a bookcase at the Government Printing Office and subjected to the natural pollution of the Washington atmosphere. The other books were returned to the laboratory, where each was carefully wrapped in waxed paper to prevent access of air, and kept in this condition until tested.

The leathers used were 21 chrome-vegetable-tanned, 2 alum-vegetable-tanned and one vegetable-tanned as follows:

Volume No.	Type	When exposed
1	Combination vegetable-chrome sheepskin	Dec. 20, 1934
2	Combination vegetable-chrome sheepskin	Jan. 11, 1935
3	Combination vegetable-chrome sheepskin	Feb. 26, 1935
4	Full chrome sheepskin	Apr. 12, 1935
5	Full chrome sheepskin	May, 1935
6	Full chrome sheepskin	Feb., 1936
7	Combination vegetable-chrome goatskin	May, 1936
8	Combination vegetable-chrome goatskin	Aug., 1936
9	Full chrome goatskin	Aug., 1936
10	Combination vegetable-chrome goatskin	Sept., 1936
11	Full chrome cowhide	March, 1937
12	Combination vegetable-chrome cowhide	Nov., 1937
13	Combination vegetable-chrome goatskin	Nov., 1937
14	Combination vegetable-chrome goatskin	Nov., 1937
15	Combination vegetable-chrome sheepskin	Dec., 1937
16	Combination vegetable-chrome cowhide	Jan., 1938
17	Combination vegetable-chrome goatskin	May, 1938
18	Full chrome goatskin	May, 1938
19	Full chrome goatskin	Aug., 1938
20	Combination vegetable-chrome cowhide	Oct., 1938
21	Vegetable-tanned eastern sharkskin	March, 1939
22	Combination vegetable-chrome sheepskin	July, 1939
23	Combination vegetable-alum sheepskin	Sept., 1941
24	Combination vegetable-alum sheepskin	Sept., 1941

The volumes exposed to atmospheric pollution were returned to the laboratory in 1953. The bindings were removed and examined. The visible effects of deterioration are reported in table I, as compared with protected bindings.

Tensile strength determinations were made of the leather from the backs of the bindings which had been exposed. The results were compared with the tensile strength of the original leathers. This introduces large sources of error. The strips of leather available allowed only 3 or 4 test samples to be taken. This small number of samples cannot be taken as representative. Another error is caused by the effects of the finish on the leather, which might give a considerable protection to the naturally exposed leather, and only slight protection to the gas chamber pieces which were exposed on all sides. A further source of error is the variation in strength between different portions of the same skin. It is improbable that the portion of the skin used for binding would be adjacent to the strip used for the original tensile strength determinations, therefore, the basis for the comparison would be faulty. In a few cases, we were able to obtain a more accurate comparison because

TABLE I

Comparison of Exposed and Protected Leathers

Color		Crackiness	
	Protected Leather	Exposed Leather	
1	Light tan	Dirty yellow	Slight
2	Light tan	Dirty brown	Not cracky
3	Cream	Brownish white	Not cracky
4	Light tan-pinkish	Dirty white	Not cracky
5	Light tan-pinkish	Dirty brown	Slight
6	Tan-pinkish	Dirty white	Not cracky
7	Bluish black	Brown	Not cracky
8	Red	Dull reddish brown	Not cracky
9	Red	Somewhat faded	Not cracky
10	Red	Somewhat faded	Slightly cracked
11	Red	Red with white undertone	Slightly cracky
			Not cracky
12	Red	Red-unaaffected	Not cracky
13	Red	Red-dull	Not cracky
14	Blue-black	Brown-black	Not cracky
15	Tan	Little changed-dull	Not cracky
16	Green	Little changed-dull	Not cracky
17	Brown	Brown-no change	Not cracky
18	Black	Black-no change	Grain slightly cracky
19	Black	Dull black	Not cracky
20	Black	Dull black	Not cracky
21	Black	Reddish black	Slightly cracky
		(red rot)	Not cracky
22	Tan	Dull tan	Very cracky
23	Red	Red (little change)	Not cracky
24	Blue	Blue (little change)	Not cracky

pieces of the original skin adjacent to the part used for the binding had been preserved, and in other cases, protected pieces from the sides of the bindings were used for control. On the whole, however, no close correlation should be expected between the comparison of tensile strengths before and after exposure.

Chemical tests consisted in the determination of pH, soluble nitrogen and total sulfur. The pH was determined by the official methods of the American Leather Chemists' Association¹. For determination of soluble nitrogen, one gram of leather was leached with 100 ml. of water at 50°C., then with N/10 Na₂CO₃ at room temperature. Soluble nitrogen is the sum of the nitrogen in the solutions expressed as a percentage of the original leather. Total sulfur was determined by the bomb method³ and reported as per cent of H₂SO₄ on the original leather.

TABLE II
Data for Deteriorated Leather

Binding No.	Cr ₂ O ₃ (1) or Al ₂ O ₃	Initial Strength Lbs./sq. in.	Deterioration		Time of Natural Exposure Years	Initial	pH		Sulfur Pickup as H ₂ SO ₄ (3)		Soluble Gas(2)		Nitrogen(3) Natural Exposure %
			Gas Chamber(2) %	Natural Exposure %			Gas Chamber	Natural Exposure	Gas Chamber	Natural Exposure	Gas Chamber	Natural Exposure	
1	3.0	1770	56.5	43.5	19	3.18	2.19	2.70	2.7	2.1	1.9	0.6	0.6
2	4.5	3420	46.3	41.2	18	4.57	2.40	2.62	3.0	1.7	0.6	0.4	0.4
3	4.6	4730	24.6	25.5	18	5.69	3.34	3.59	1.5	1.7	0.3	0.7	0.7
4	4.9	1850	27.7	31.7	18	4.34	2.75	3.34	1.7	1.1	0.2	0.7	0.7
5	3.4	4130	40.7	58.3	18	4.33	3.13	3.28	2.6	2.2	0.1	0.6	0.6
6	4.6	3450	10.6	19.0	17	4.95	2.93	3.50	1.0	1.5	0.3	0.6	0.6
7	2.0	5350	51.4	70.3	17	3.48	2.27	2.42	4.2	1.2	1.4	1.1	1.1
8	2.2	4950	50.2	62.4	17	4.45	2.23	2.75	4.6	1.5	0.6	0.7	0.7
9	4.3	6300	32.5	21.8	17	4.04	2.75	3.02	2.4	1.5	0.1	0.4	0.4
10	2.5	2530	39.5	56.9	17	4.33	2.53	2.55	2.1	2.3	0.8	1.7	1.7
11	3.0	2690	18.9	20.8	16	4.34	3.30	3.45	1.6	0.9	0.3	0.8	0.8
12	2.2	1370	28.7	6.1	16	3.79	2.27	3.20	3.6	2.4	0.5	0.4	0.4
13	2.5	6180	55.8	65.5	16	3.32	2.14	2.60	3.9	1.9	0.7	0.4	0.4
14	2.3	5740	51.7	61.3	16	3.39	2.25	2.58	3.7	2.0	0.9	0.3	0.3
15	1.1	2170	45.5	45.0	16	3.51	2.13	2.90	3.6	2.0	1.1	0.5	0.5
16	1.9	2630	52.9	31.5	15	4.07	2.26	3.10	2.9	1.9	1.7	0.5	0.5
17	1.0	5620	78.5	35.5	15	6.08	2.17	2.95	4.9	1.7	1.8	0.6	0.6
18	4.7	4600	25.1	53.9	15	4.17	2.73	2.92	3.9	2.8	0.5	0.5	0.5
19	2.7	7020	38.3	40.3	15	5.14	2.40	2.97	3.5	1.2	0.4	0.4	0.4
20	0.9	2010	46.4	36.8	15	3.28	2.16	2.93	3.7	2.5	0.7	0.4	0.4
21	None	1050	71.4	61.9	15	3.18	2.16	2.21	4.0	3.1	4.9	3.3	3.3
22	2.1	2670	46.5	65.9	14	3.12	2.14	2.65	3.2	2.1	0.8	0.5	0.5
23	2.3	1770	10.3	22.6	12	4.11	3.56	3.90	1.9	0.7	0.3	0.4	0.4
24	2.3	2680	7.1	7.9	12	4.16	3.60	3.92	1.0	1.5	0.2	0.3	0.3

(1) Leather 21 was vegetable tanned; 23 and 24 vegetable leathers retanned with alum; the rest of the leathers are chrome or combination chrome vegetable leathers.

(2) Gas chamber data are for 12 weeks exposure.

(3) Calculated as per cent of original leather.

Table II gives the results of the physical and chemical tests as compared with similar results obtained on the leather exposed in the gas chamber for 12 weeks.

DISCUSSION

The exposure period of the bindings ranged from 12 to 19 years. Therefore, a ranking of the volumes for durability is not absolutely accurate, but the results should be fairly conclusive. In the following table the volumes are ranked in the order of decreasing resistance as shown by the gas chamber and by atmospheric exposure.

Ranking of Leather in Order of Decreasing Resistance as Measured by Tensile Strength

Volume No.	Ranking Gas Chamber	Bindings	Volume No.	Ranking Gas Chamber	Bindings	Volume No.	Ranking Gas Chamber	Bindings
1	22	14	9	9	5	17	24	10
2	14	13	10	11	18	18	6	16
3	5	7	11	4	4	19	10	11
4	7	9	12	8	1	20	15	12
5	12	17	13	21	22	21	23	20
6	3	3	14	19	19	22	16	23
7	18	24	15	13	15	23	2	6
8	17	21	16	20	8	24	1	2

TABLE III
Evaluation of Ranking Data

To evaluate the data we used a nonparametric test proposed by Kendall and Smith³³, as modified by the Frankford Arsenal¹⁴.

The relative rankings and their sums were taken as follows:

Gas Chamber	22	14	5	7	12	3	18	17	9	11
Natural Exposure	14	13	7	9	17	3	24	21	5	18
Sum	36	27	12	16	29	6	42	38	14	29
4	8	21	19	13	20	24	6	10	15	23
4	1	22	19	15	8	10	16	11	12	20
8	9	43	38	28	28	34	22	21	27	43
										39
										8
										3

$$\text{The mean is } \frac{m(n+1)}{2} = \frac{2(25)}{2} = 25$$

where m = number of methods of test = 2 (gas chamber and natural exposure).

n = number of samples = 24

S — sum of the squares of the differences between the mean and the separate

sums = $11^2 + 2^2 + 13^2 - \text{etc.} = 3806$

$$w = \frac{12s}{m^2(n^3-n)} = 0.827$$

The Snedecor F value was calculated as proposed by the Frankford Arsenal Manual.

$$F = \frac{A}{B} \quad \text{Where } A = (n-1)w \text{ and } B = l-w.$$

$$\frac{A}{B} = 109.9$$

$$\text{The degrees of freedom for } A = (n-1) - \frac{2}{m} = 22$$

$$\text{The degrees of freedom for } B = (m-1) (n-1) - \frac{2}{m} = 22.$$

From the table the F values for the 5% and 1% level are: $F_{.05} = 2.05$ $F_{.01} = 2.79$
A comparison of these values with the F value as determined indicates that there is good agreement between the two methods of test.

A non-parametric analysis of these results (table III) shows a Snedecor F value of 109.9 as compared with 2.05 at the 5 per cent level and 2.79 at the 1 per cent level. This shows good agreement between the two test methods. Table II shows that sulfur pick-ups are close to what would be predicted.

Corroborating results of previous tests, it is seen that the amount of soluble nitrogen for semi-chrome or alum leathers is not a satisfactory criterion of deterioration. All pH figures for the exposed bindings are higher than anticipated. We can give no satisfactory explanation for this.

The results of the two alum-retanned leathers are of particular interest. Although the exposure period is not as long as for some of the other leathers, it is still long enough to give a fair indication of the value of the tannage. The deterioration is small, as predicted by gas chamber tests. As measured by the peroxide test or the bomb test, the resistance of this type of leather is low.

In considering the mechanism of the deterioration of leather exposed to atmospheric pollution, it has been established that the leather absorbs sulfur dioxide from the air, which is oxidized in the leather to sulfuric acid. This oxidation may be accelerated by the presence of iron or other metals. The sulfuric acid degrades the protein by hydrolysis which is accompanied by oxidation. It has been assumed that oxidation as well as hydrolysis is necessary to produce the deterioration. This assumption is supported by the fact that oxidation as well as hydrolysis is required to give to deteriorated vegetable leathers the typical appearance of "red rot". Further, the amount of ammonia produced is too large to be accounted for by simple hydrolysis without oxidation. However, these facts can be as satisfactorily explained by assuming that oxidation is a secondary phenomenon acting only on proteins partly degraded by hydrolysis. In support of this assumption, it is found that mineral tanned leather or combination mineral-vegetable tanned leather may undergo as much as 40 per cent deterioration with the formation of only negligible amounts of ammonia. In this case, only small amounts of soluble nitrogen are formed. This is explained by Kuntzel³⁵ as follows: "It is probable that this decomposing action is not limited only to the splitting

of soluble protein fragments from the insoluble protein system but that also the insoluble remainder of the fibre system undergoes decomposition, leading to a diminution of tensile strength. On this view, in the course of the acid action the collagen undergoes a mild hydrolytic fission of such a nature that the whole system of molecules, bound by main and auxiliary valences, does not as such fall to pieces."

The results of the gas chamber test do not depend upon any assumption regarding the mechanism of the reaction involved. The only assumption made is that in accentuating the normal conditions of atmospheric pollution, the reactions involved will proceed in the same course at an accelerated rate. The gas chamber gives very valuable results in evaluating the results of leather treatments where the treatment is the only variable involved. The results are not as satisfactory in comparisons of different leathers, where other factors, such as thickness or different types of protective coatings, are involved.

Two methods have been devised for evaluating the resistance of leather to acid deterioration based on the assumption that oxidation is the principal factor in the action. In the method of Innes²⁴ sulfuric acid is added to leather in a sufficient quantity to give 5 per cent on the weight of the dry leather. After drying, hydrogen peroxide is added, in 6 additions, with intermediate drying in the proportion of 0.6 ml of 10 volume hydrogen peroxide per gram of leather. Deterioration is judged by cracking, blackening, gelatinization or the production of holes in the leather.

In the method devised by Kanagy²⁷, of the U. S. Bureau of Standards, leather is heated to 100°C. in an oxygen bomb, without any addition of acid.

A comparison of the peroxide, gas chamber, and oxygen bomb methods was published in 1944¹³. This was the result of collaborative work between the British Leather Manufacturers Association, represented by R. F. Innes; the Bureau of Chemistry and Soils of the U. S. Department of Agriculture, represented by R. W. Frey, C. W. Beebe, and J. S. Rogers; and the Bureau of Standards of the U. S. Department of Commerce, represented by R. C. Bowker and J. R. Kanagy. The conclusions derived from this comparison were:

1. "Acid deterioration is the main cause for the failure of leathers normally expected to give many years of service. If the leather is made with a sufficiently high pH and no further acid has been deliberately added, then the acid causing deterioration evidently has been absorbed from polluted atmospheres.
2. "The rate of deterioration of leathers resulting from the absorption of acids from the atmosphere is dependent upon three main factors: (a) rate of absorption of acid from air, which may be greatly influenced by methods

of finishing, (b) effect of absorbed acid in reducing the pH of the leather, in which action differences in buffering capacity play an important part, and (c) the rate of action of the acid on leather at a definite pH. Each of these factors varies with different leathers.

3. "The gas chamber test is the most satisfactory method for measuring resistance to acid deterioration, but cannot be used to evaluate deterioration caused by other factors. Theoretically, the criterion of percentage soluble nitrogen should be the basis of assessment since it indicates breakdown of the tanned collagen, but loss in tensile strength is found practically to be superior if enough of the sample is properly selected and used. It is a more sensitive criterion since a measurable loss in tensile strength may be observed before the sample has deteriorated sufficiently to give a measurable change in the amount of nitrogenous material extractable. It has also been shown that combination leathers give abnormally low values in soluble nitrogenous materials, and, in the case of leathers tanned partly or wholly with chromium, alum or other mineral agents, it is thought that the loss in tensile strength indicates most nearly the correct degree of deterioration.
4. "There is a marked parallelism in the durability of the leathers as judged by the gas chamber and peroxide tests. Both show that sodium lactate, formate and chloride have a marked protective action but the peroxide test has its limitation, particularly in that it causes an unequal distribution of acid in the leather. It is also of no use for combination chrome-vegetable leathers which are growing in importance on account of their durability. The peroxide test gave much deterioration because it introduced more mineral acid than that which was absorbed by this particular leather in the gas chamber test.
5. "Oxidation tests determine reactivity of leather to oxygen under standard conditions and the rate of oxidation apparently varies under different conditions. The reactivity to acid is not necessarily the same as the reactivity to oxygen. No account is taken of the presence of buffering materials which actually neutralize acid as it is absorbed and no account is taken of the rate of absorption of acid. Thus, the oxygen bomb test is not satisfactory as a forecast of durability in acid atmospheres because the leathers do not become acid and it gives quite different results from the other two tests. The native tanned Nigerian goatskin shows less deterioration after removing the water solubles. The quebracho-tanned leather shows as good durability as the sumac-tanned leather. These findings are at variance with practical experience and published research in this connection.
6. "Buffering capacity is no criterion of durability. The following table (for table see original text)¹³ shows that resistance to the gas chamber and

peroxide tests does not run parallel with buffering capacity. This might be expected because durability is also determined by the rate of absorption of acid from the air and the rate of action of the acid on leather at a definite pH. Buffering capacity also does not take in account protection provided by such materials as sodium chloride which do not affect pH, reactivity or rate of absorption."

The explanation of the fifth conclusion is that this test was devised for a normal atmosphere and not for one containing acid fumes. Kanagy¹³ states "We recognize the damaging effects of sulfur dioxide fumes but we believe that by using leather having a satisfactory initial pH and with the aid of modern methods of air conditioning this factor can be practically eliminated." Burton took issue with this statement as far as England is concerned with the opinion that sulfur dioxide pollution was still a major problem. It is our opinion that in this country also atmospheric pollution is a major problem of increasing importance and many bookbindings are not protected by air-conditioning. If results from these tests are extended to upholstery leather, the protection given by air-conditioning is of a still smaller extent.

Innes, Mayer and Mitton have tested 8 leathers in their gas chamber²⁶. In the comparison of the leathers after exposure, alum-treated leather ranked first by gas chamber tests, but only sixth by the peroxide or bomb test. As the rating given by their gas chamber confirms the results of our gas chamber, and further, as these results are corroborated by the actual exposure tests reported in this paper, it would appear that the ratings given by the peroxide or bomb tests are erroneous. Apparently, the peroxide test is unsatisfactory for vegetable-alum leathers as well as for chrome-vegetable leathers.

CONCLUSIONS

Results of actual exposure of leather for 11 to 19 years confirm reasonably closely the predictions made by gas chamber tests of the original leather.

The soluble nitrogen content of deteriorated combination vegetable and mineral leather is not a satisfactory criterion of the amount of deterioration.

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